



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number:

0 424 833 A2

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 90120173.1

⑭ Int. Cl. 5: C08J 5/04, C08G 61/08

⑮ Date of filing: 20.10.90

⑯ Priority: 24.10.89 US 426390

⑰ Date of publication of application:
02.05.91 Bulletin 91/18

⑱ Designated Contracting States:
BE DE DK FR GB IT NL SE

⑲ Applicant: THE B.F. GOODRICH COMPANY
3925 Embassy Parkway
Akron Ohio 44313-1799(US)

⑳ Inventor: Goodall, Brian L.
3959 Clover Hill Road
Akron, Ohio 44313(US)
Inventor: Standish, John V.
4615 Broadale Road
Cleveland, Ohio 44109(US)

㉑ Representative: von Kreisler, Alek,
Dipl.-Chem. et al
Patentanwälte Von Kreisler-Selting-Werner,
Delchmannhaus am Hauptbahnhof
W-5000 Köln 1(DE)

㉒ Coated reinforcing material.

㉓ This invention pertains to a substrate having thereon a coating of a metathesis catalyst and/or cocatalyst, to a method for applying such a coating to the substrate, and to a process for producing a molded product by placing into a mold a substrate having thereon a coating of the metathesis catalyst and/or cocatalyst, introducing into the mold at least one norbornene-type monomer, polymerizing the monomer in presence of the metathesis catalyst system, and extracting the molded article from the mold wherein the monomer(s) is polymerized to a thermoset or crosslinked polymer.

COATED REINFORCING MATERIAL

Background of Invention

5 The prior art polymerization of a norbornene-type monomer in the presence of a metathesis catalyst system is characterized by ring opening of the monomer and formation of a polymer that can have pendant unsaturation in the cyclic structure. Physical properties can be further enhanced by using a catalyst component which further cleaves another cyclic structure in the polymer.

10 The prior art polymerizations are generally carried out in bulk in substantial absence of a solvent for the norbornene-type monomer or a mixture thereof. Such a process is referred to as reaction injection molding or RIM and results in a thermoset polymer which is polymerized in a mold and extracted therefrom in a short period of time such as one quarter of an hour, preferably less than one minute, depending on the size of the article extracted from the mold. Such a method is characterized by combining a plurality of reactant streams, one containing the catalyst of the metathesis catalyst system and a second containing the cocatalyst, and at least one stream containing a norbornene-type monomer or a mixture thereof; and then 15 injecting the mixed streams into a mold where polymerization results in a tough, rigid thermoset polymer with high flexural modulus and excellent impact strength.

15 Reinforcing agents or fillers have been used in the past in making reinforced polynorbornene products. These are materials which can increase the polymer's flexural modulus with only a small sacrifice in impact resistance. Possible reinforcing agents and fillers include glass fibers, wollastonite, mica, carbon black, talc and calcium carbonate. The amount of such agents can vary up to 75%, based on the weight of the final product, preferably 1 to 40% by weight. The addition of reinforcing agents and is also known to decrease shrinkage of the molded product.

20 There are differences between particulate fillers and reinforcing agents. Examples of fillers are calcium carbonate, talc, clays, carbon black, and the like whereas examples of reinforcing agents are minerals such as wollastonite and fibers such as aramid, graphite, polyethylene, vegetable, glass, and the like, especially glass. Fillers are normally used as bulking agents to reduce cost of the final product whereas reinforcing agents are used with the primary objective to improve physical properties of the final product. It is intended here to cover both. Product cost can also be reduced by using fillers and/or reinforcing agents in the final product. For purposes herein, the term "substrate" denotes both reinforcing agents and fillers.

25 In conducting the RIM polymerization discussed herein, the catalyst and cocatalyst are kept in separate tanks to prevent initiation of polymerization. Polymerization commences violently when catalyst and cocatalyst are brought together. By using modifiers with cocatalysts, a less violent polymerization at a more uniform rate can be carried out. Such modifiers include ethers, esters, ketones and nitriles.

30 There is another way to attenuate or lessen the action of the metathesis cocatalyst in order to carry out the polymerization. By introducing an alkoxy or aryloxy group into the alkyl aluminum halide cocatalyst, it is thus possible to diminish or reduce the reducing power thereof so that controlled polymerization can be conducted.

40

Summary of Invention

45 This invention pertains to a substrate having a metathesis catalyst component(s) on its surface and to a process for making a reinforced polynorbornene product by introducing a substrate into a mold, the substrate material having thereon a metathesis catalyst component(s), introducing a monomer mixture into the mold, the monomer mixture containing at least one norbornene-type monomer, and if necessary, introducing the other metathesis catalyst component; allowing the norbornene monomer(s) to polymerize by ring opening to form a thermoset polynorbornene type product, and extracting the product from the mold.

50

Detailed Description of Invention

The gist of this invention resides in applying a metathesis catalyst or cocatalyst component or a mixture thereof to a substrate. The catalyst and/or cocatalyst component is preferably insensitive to air and oxygen

and can be applied to the substrate from an aqueous or an organic medium in which the component may or may not be soluble. The component can be applied to the substrate by itself or in another composition, such as a sizing solution. By the use of this invention, a molder can place a substrate coated with a catalyst or cocatalyst into a mold, introduce the monomer solution into the mold whereby the monomer solution would flow around the coated substrate, and extract a thermoset molded product from the mold. In this manner, the need for a separate monomer stream containing the catalyst or cocatalyst is obviated as well as the need to mix the catalyst stream with the cocatalyst stream before injecting the mixed streams into the mold.

The reinforcing or filler material, or substrate, may be glass, graphite, aramid fibers, wollastonite, mica, carbon black, talc, calcium carbonate or mixtures thereof. For example, the reinforcing material can be in the form of mats made of a continuous strand of glass fiber with a density of 1.5-2.0 oz/ft.², such as random glass mat OCF 8608 or random glass mat OCF 8610 from Owens Corning Fiberglas Corporation. To obtain even greater reinforcement, mats of graphite fibers or Kevlar aramid fibers can be used. Examples of these are mats of woven AS-4 or AS-6 graphite fibers of density 1.0-1.5 oz/ft² from Hercules Incorporated.

Preferably, the mat is made up of fibrous material which is woven, intertwined or interlaced. Due to such weaving, intertwining or interlacing, the fibers of the mat are substantially interdependent in their response to forces applied to the mat. The mat can be made, for example, from chopped rovings by pulling vacuum while spraying chopped rovings and a binder solution onto a shaped screen which can then be passed through a heated tunnel or oven to set the polymeric binder on the chopped rovings. Other types of mats include woven roving, random mats, needled mats, and preformed shapes made by such processes.

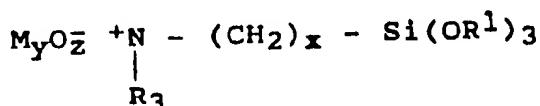
The fiber mats can be made from long fibers or from short fibers. Long or continuous fibers are generally considered to be about 2 inches in length and longer whereas short fibers are generally considered to be about 2 inches and shorter. Continuous glass fiber mats are known which are 110 inches wide and are made from chopped strands about 2 inches long.

Therefore, in accordance with the invention disclosed herein, a glass fiber mat can be dipped in a solution or dispersion of the catalyst and/or cocatalyst to obtain a glass fiber mat that is virtually indistinguishable from the original mat but containing sufficient level of the catalyst and/or cocatalyst in another medium in which it is soluble or insoluble. The solvent or medium is removed by drying before the mat is ready for use. The catalyst and/or cocatalyst level can be adjusted by varying concentration of the catalyst and/or cocatalyst in a medium, be it organic, inorganic or aqueous. The catalyst and/or cocatalyst level can also be adjusted by varying other process parameters, such as the dipping period which can be 1/4 of a minute or less.

The catalyst and/or cocatalyst can also be incorporated in a sizing for the substrate. Traditional sizings for glass are applied as water solutions or dispersions. Sizings are applied to substrate, such as glass fibers, because glass fibers are very fragile and need a sizing agent. Sizings often contain organosilanes such as vinyl triethoxy silane or styryl triethoxy silane or methacryl triethoxy silane or gamma-aminopropyl triethoxy silane. When fiber mats are made, a binder is required to provide the mat with handling strength. These binders are typically a polyester powder which is sprayed onto the mat and then heated to melt the powder. After cooling, the powder binders based on polymers tack or bind the mat together. Alternately, latexes, such as acrylic latexes, and polyester emulsions, have been used.

The catalyst and/or cocatalyst and the binder can be included in a sizing formulation. Such sizings include a metathesis catalyst and/or cocatalyst, an organic silane to act as a coupling agent for the substrate, a lubricant to improve handling of the coated substrate, an antistatic agent to reduce the static electricity on the treated substrate, a film former to act as a binder for the substrate if a mat is to be prepared, and other optional ingredients to improve the substrate in whatever form it may be used.

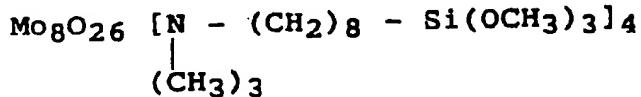
To improve coupling of the metathesis catalysts and/or cocatalysts to the substrate, especially when the substrate contains glass, silica, or alumina, the catalysts and/or cocatalysts can be provided with at least one silyl moiety. Such modified catalysts, for example, can be selected from silyl organoammonium molybdates and tungstates and can have the following formula:



55

where x is 1 or larger, M is molybdenum (Mo) or tungsten (W), and y and z are chosen to give active

5 molybdate or tungstate moiety. A specific example of such silyl catalysts is trimethoxysilyloctyltrimethylammonium molybdate, which has the following formula:



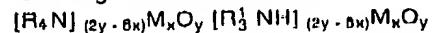
10 The advantage of such silyl organoammonium molybdates and tungstates is that they can be used to support or affix the catalyst to a substrate, especially a substrate containing silica, glass, alumina, or the like. The silyl molybdates and tungstates can be synthesized in an alcohol or through a route in which the Si-OR groups are not hydrolyzed.

15 The catalyst and/or cocatalyst solution or dispersion, applied from a sizing formulation or otherwise, can also contain other components. Examples of such other components include elastomers, blowing agents, fillers, flame retardants, and the like.

20 The ring-opening metathesis catalyst system is composed of a metathesis catalyst component and a metathesis cocatalyst component, or catalyst and cocatalyst. The known ring-opening metathesis catalyst systems for use in bulk polymerization of norbornene-type compounds are acceptable herein. Examples of the catalysts include halides, oxyhalides, oxides and organic salts of tungsten, molybdenum, and tantalum. 25 Specific examples of the catalysts include tungsten hexachloride, tungsten oxytetrachloride, tungsten oxide tridodecylammonium tungstate, methyltricaprylammonium tungstate, tri(tridecyl) ammonium tungstate, trioctylammonium tungstate, molybdenum pentachloride, molybdenum oxytrichloride, tridodecylammonium molybdate, methyltricaprylammonium molybdate, tri(tridecyl)ammonium molybdate, trioctylammonium molybdate, and tantalum pentachloride. It is preferred to use catalysts which are soluble in one or a mixture of norbornene-type monomers. From this viewpoint, organoammonium molybdates and tungstates are used.

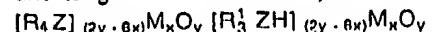
30 If the catalyst is a halide, it can be solubilized in one or a mixture of the norbornene-type monomers by pretreatment with an alcoholic or a phenolic compound. Furthermore, if necessary, complexing agents can be used in combination therewith. Examples of the complexing agents include benzonitrile, tetrahydrofuran, and other Lewis bases, acetyl acetone, and alkyl esters of acetoacetic acid. By doing this, pre-polymerization can be prevented.

35 The organoammonium molybdates and tungstates suitable herein as metathesis catalysts have the following structural formulas:



40 where M is molybdenum or tungsten; O represents oxygen; x and y represent the number of M and O atoms in the molecule based on the valence of +6 for molybdenum, +6 for tungsten, and -2 for oxygen; and R and R' radicals can be same or different and are selected from hydrogen, alkyl and alkylene groups of 1 to 20 carbon atoms, and cycloaliphatic groups each of 5 to 10 carbon atoms. These catalysts are insensitive to air and moisture.

45 Other metathesis catalysts suitable herein include organoarsonium and organophosphonium molybdates and tungstates. These catalysts are characterized by the following structural formulas:



50 where Z is the element arsenic or phosphorus; M is molybdenum or tungsten; O represents oxygen; x and y represent the number of M and O atoms in the molecule based on the valence of +6 for molybdenum, +6 for tungsten, and -2 for oxygen; and R and R' radicals can be same or different and are selected from hydrogen, alkyl and alkylene groups of 1 to 20 carbon atoms, and cycloaliphatic groups each of 5 to 10 carbon atoms. These catalysts are also insensitive to air and moisture.

55 Still other metathesis catalysts suitable herein include the organoammonium, organophosphonium and organoarsonium heteropolymolybdates and heteropolytungstates. These catalysts are also insensitive to air and moisture.

The metathesis catalyst for ring-opening polymerization of a norbornene-type monomer or a mixture thereof is used at a level of 0.05 to 1 weight part based on 100 weight parts of all norbornene-type monomers, preferably 0.1 to 0.7 weight part.

60 The cocatalysts or activators are selected from the organoaluminums such as trialkylaluminums, alkylaluminum hydrides, alkylaluminum halides, alkoxyalkylaluminum halides, aryloxyalkylaluminum halides, and metalloxyalkylaluminum halides; organic tin compounds; and organic lead compounds. The alkylaluminum halide cocatalysts initiate polymerization immediately upon mixing thereof with a metathesis catalyst. Initiation of polymerization can be delayed by using a modifier selected from esters, ethers,

ketones, and nitriles, as is well known in the art, especially ethyl benzoate, butyl ether, or diethylene glycol dimethyl ether.

Preferred metathesis cocatalysts are selected from the alkoxyalkylaluminum halide and aryloxyalkylaluminum halide cocatalysts defined as follows:

6 (RO)_a R_b¹ AlX_c

where R is selected from alkyl and phenyl radicals, R¹ is selected from alkyl radicals; X is a halogen; the sum of a, b and c is 3.0 and each one of these parameters defines the equivalents of the moieties in the cocatalyst. This group of preferred cocatalysts includes alkoxyalkylaluminum chlorides and iodides and phenoxyalkylaluminum chlorides and iodides, especially propoxyethylaluminum chloride and the sesquichloride. The alcohol can be added separately from the alkylaluminum halide cocatalyst and the alcohol reacts in situ to form the final cocatalyst. These cocatalysts are soluble in norbornene-type monomer or mixtures thereof and can have a variable pot life depending on the amount of alcohol or the alkoxy moiety used to moderate it. The more alcohol used the longer is the pot life of the system using the alkoxyalkylaluminum or phenoxyalkylaluminum halide cocatalysts.

15 Preferred metathesis cocatalysts also include metaloxyalkylaluminum halides defined as follows:

(R_nMO)_a R_b¹ AlX_c

where M is a metal selected from tin, lead, and aluminum; R and R¹ are individually selected from organic groups, especially lower alkyl groups and phenyl groups, n is 2 or 3, depending on the metal; X is a halide; and the sum of a, b and c is 3.0, each parameter defining the equivalents of the moieties in the cocatalyst.

20 Also included in the preferred metathesis cocatalysts are the organic tin compounds selected from alkyltin cocatalysts of lower alkyl tetraalkyltins, such as tetrabutyltin, lower alkyl trialkyltin and triaryltin hydrides such as tributyltin hydride, triphenyltin hydride, trimethyltin hydride, triethyltin hydride, tripropyltin hydride, tetraethyltin, tetrabutyltin, and the like. Also preferred are the organic lead compounds selected from alkyllead cocatalysts such as tetraethyllead. These cocatalysts are insensitive to air and moisture and can be handled in air without special precautions which are needed with the alkoxy and aryloxy alkylaluminum halides and the other metathesis cocatalysts.

25 The metathesis cocatalysts that are air insensitive can be applied to the reinforcing material from an organic or aqueous medium or be included in a sizing composition. The resulting air and moisture stable reinforcing material, especially glass fibers, can be used in the manufacture of structural polymeric matrix composites where the polymer matrix is partly or wholly composed of polymerized norbornene-type monomer or a mixture thereof. Same or similar conclusions apply to reinforcing material coated with a metathesis catalyst.

30 There are metathesis catalyst and metathesis cocatalyst systems which can be combined at room or ambient temperature without reacting or causing initiation of polymerization. Such catalysts and cocatalysts can be applied to a substrate from organic or aqueous systems in predetermined amounts. Such treated substrate is then placed in a mold, a norbornene monomer or a mixture thereof is introduced into the mold around the substrate, and the temperature of the mold contents is increased to polymerize the monomer(s). This approach has limited application due to the need for special metathesis catalysts and metathesis cocatalysts which are inert to each other at room or ambient temperature but which initiate polymerization 40 at an elevated temperature.

35 As noted above, suitable metathesis catalysts and cocatalysts can be applied to a substrate from an organic or an aqueous system. Suitable solvents for use in the organic systems include aliphatic and cycloaliphatic hydrocarbon solvents such as pentane, hexane, heptane, octane, cyclohexane, cyclohexene, cyclooctane and the like; aromatic hydrocarbon solvents which are liquid or easily liquified such as benzene, toluene, naphthalene and the like; and substituted hydrocarbons wherein the substituents are inert, such as dichloromethane, chloroform, chlorobenzene, dichlorobenzene, and the like. Aqueous systems devoid of flammable and volatile organic solvents offer benefits in certain commercial operations.

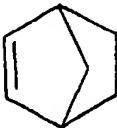
45 Whether applied from an organic or an aqueous system, the catalyst or cocatalyst deposits on the substrate and becomes insoluble or difficult to leach out in organic and other solvents. This approach requires that the molder introduce into a mold a monomer charge with a catalyst or cocatalyst over the treated substrate whereby the monomer charge in liquid form flows around the treated substrate to fill all voids and wet the substrate.

50 It is preferred to select cocatalysts which are soluble in the norbornene-type monomer and mixtures thereof and which are relatively insensitive to oxygen and moisture. Between 0.1 and 100 millimoles, preferably 0.2 to 50 millimoles, of the metal in the cocatalyst is used per mole of norbornene-type monomer or a mixture thereof.

The norbornene-type monomers or polycycloolefins that can be polymerized in accordance with the process described herein are characterized by the presence of at least one norbornene group. Identified by

formula I, that can be substituted or unsubstituted:

5



I

10 Pursuant to this definition, suitable norbornene-type monomers include polycycloolefins and in particular tricyclic and higher cyclic olefins selected from substituted and unsubstituted norbornenes, dicyclopentadienes, dihydrodicyclopentadienes, trimers of cyclopentadiene, and tetracyclododecenes. Examples of preferred monomers referred to herein include dicyclopentadiene, tetracyclododecene, methyltetracyclododecene, hexacycloheptadecene, methyl hexacycloheptadecene, 2-norbornene and other norbornene monomers such as ethyldenenorbornene, vinyl norbornene, 5-methyl-2-norbornene, 5,6-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-butyl-2-norbornene, 5-hexyl-2-norbornene, 5-octyl-2-norbornene, and 5-dodecyl-2-norbornene.

15 The invention especially contemplates preparation of homopolymers, copolymers and terpolymers of norbornene, methylnorbornene, vinyl norbornene, ethyldenenorbornene, dicyclopentadiene, tetracyclododecene, methyltetracyclododecene, hexacycloheptadecene, and methyl hexacycloheptadecene.

20 The monomer or a mixture of norbornene-type monomers can contain up to about 20%, preferably 1 to 10%, by weight thereof of at least one other copolymerizable monomer. Such other copolymerizable monomers are preferably selected from mono- and dicyclopentadienes containing 4 to 12 carbon atoms, preferably 4 to 8 carbon atoms, examples of which include cyclobutene, cyclopentene, cyclopentadiene, 25 cycloheptene, cyclooctene, 1,5-cyclooctadiene, cyclodocene, cyclododecene, cyclododecadiene, and cyclododecatriene.

30 In addition to the metathesis catalyst or cocatalyst in the monomer solution or an organic solvent solution or in an aqueous dispersion, in the preferred embodiment where a metathesis catalyst or cocatalyst is deposited on the substrate, a halogen source can be used in amount of 0.1 to 2 millimoles thereof per mole of the norbornene-type monomer(s).

35 Suitable halogen source herein is any halogen compound which can provide sufficient halogen for polymerization of one or more norbornene-type monomers in the presence of the metathesis catalyst system disclosed herein. Such halogen source is generally selected from non-aluminum metal halides where the metal is selected from tin, antimony, germanium and silicon. Depending on the valence of the metal, the compound suitable herein as a halogen source can contain a full complement of a halogen or it can contain a lesser number of halogen atoms in which case, the remaining valence or valences are satisfied by a group selected from hydrogen, alkyl and alkoxy groups containing 1 to 6 carbon atoms, and phenyl and alkylphenyl groups containing 6 to 14 carbon atoms.

40 Examples of a suitable halogen source are chlorosilanes selected from dimethylmonochlorosilane, dimethyldichlorosilane, diphenyldichlorosilane, tetrachlorosilane, and the like. Tetrachlorosilane is particularly preferred.

45 In the monomer stream, other ingredients can be used such as elastomers, blowing agents, fillers, flame retardants, and the like.

In the present invention, an elastomer may be used together with the catalyst or cocatalyst, but preferably with the cocatalyst. The elastomers which can be used are natural rubber, polybutadiene, styrene-butadiene copolymer, polyisoprene, styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, ethylene-propylene-diene terpolymer, ethylene-vinyl acetate copolymer, and their 50 hydrides. The elastomers may be used alone or as a mixture of two or more.

If a solution containing a monomer has low viscosity, the viscosity of such solution can be properly adjusted by dissolving elastomer therein.

55 The blending ratios of these elastomers are ordinarily 0.5-20 parts by weight, preferably 1-15 parts by weight, with respect to 100 parts by weight of the monomer charge. If the blending ratio of the elastomer is too low, the effect of rendering the impact resistance will be small. On the other hand, if it is too high, the viscosity of the solution will be too high and the molding operability will be poor.

The best mode now contemplated of carrying out this invention is exemplified by the following working examples of preferred specific embodiments. This invention is not limited to these specific examples. All percentages are by weight, based on the weight of monomer charge, unless otherwise clearly indicated.

Example 15 Preparation of Catalyst

In this catalyst preparation, ADOGEN 340 (commercially available from the Sherex Corporation) was used. This material is a long chain fatty amine with a composition NR_3 where R comprises 5% $C_{14}H_{29}$, 30% $C_{16}H_{33}$ and 65% $C_{18}H_{37}$.

10 A. 10 grams ADOGEN 340 was weighed into a 1000 ml round bottomed flask to which 100 ml methylene chloride was added to yield a colorless solution.

B. 13.22 grams ammonium molybdate $[(NH_4)_2Mo_2O_7 \cdot 4H_2O]$ was dissolved in 200 ml distilled water to yield a light blue solution.

15 C. 6.24 grams hydrochloric acid (37%) was diluted with 20 ml distilled water to yield a colorless solution.

D. With stirring, solution B was added to solution A, and thereafter, solution C was added to the resulting solution. On mixing, the methylene chloride layer became light yellow in color. This color intensified somewhat after refluxing for 1 hour. The methylene chloride layer was separated off, washed twice with distilled water and dried, whereby the catalyst $(R_3NH)_4Mo_8O_{26}$ was obtained (R as described above) as a yellow-brown waxy solid.

Preparation of Coated Glass Fiber

25 Six grams of the above-described organoammonium molybdate was dissolved in 400 g methylene chloride in air. A section of commercially sized Owens Corning 8808 fiber glass weighing 30.41 g was dipped into this solution for 30 seconds and then allowed to air dry to constant weight. The final weight of the catalyst coated glass fiber mat was 30.70 g, indicating a catalyst loading of 0.29 g. The coated glass fiber mat was completely dry to the touch.

30

Preparation of Cocatalyst Solution

35 To a 92.5/7.5 weight mixture of dicyclopentadiene (DCPD) and ethyldenenorbornene (ENB) (131.3 g) was added under nitrogen n-propanol in amount of 3.6 ml of a 1.0 molar solution in a DCPD/ENB mixture followed by diethylaluminum chloride (DEAC, 6 ml of a 0.5 molar solution in a DCPD/ENB mixture and silicon tetrachloride (6 ml of a 0.25 molar solution in a DCPD/ENB mixture).

40 Polymerization

The section of catalyst-coated glass fiber mat was placed into a 9" x 6" x 1/8 inch aluminum cavity mold. The mold was flushed with nitrogen and heated to 80°C. The cocatalyst solution was then introduced to fill the mold around the coated glass fiber mat. There was an immediate exotherm which peaked after 45 seconds at 143°C. After cooling, the mold was opened to reveal a hard, completely solidified glass fiber reinforced plaque weighing 97.20 g, approximately 31% by weight glass fiber.

Example 2

50

Preparation of Coated Glass Fiber

55 Three grams of tristridecylammonium molybdate $\{[(C_{13}H_{27})_3NH\}_4Mo_8O_{26}\}$ was dissolved in 200 g methylene chloride under air. A section of Owens Corning 8808 glass fiber mat weighing 41.0 g was dipped into this solution for 30 seconds and then allowed to air dry to constant weight. The final weight of the coated mat was 41.3 g, indicating that 0.3 g of the catalyst had been adsorbed onto the glass fiber mat.

The mat was a very pale green in color and slightly tacky to the touch.

Preparation of Cocatalyst

6 The cocatalyst component used was stored in a 5-gallon "Firestone type" can under a pressure of 30 psi nitrogen. The solution comprised 8323 g, 92.5/7.5 DCPD/ENB mixture in which had been dissolved a commercially available Kraton D-1102 elastomer in amount of 317 g. To this solution under nitrogen was added neat 44.65 g diethylaluminum chloride, 32.05 g of 2,4-dimethyl-3-pentanol in 288.5 g of 92.5/7.5 DCPD/ENB mixture, 3.46 g n-propanol in 31.1 g of 92.5/7.5 DCPD/ENB mixture, and 31.46 g neat SiCl_4 .

10

Polymerization

15 The section of catalyst-coated glass fiber mat was placed into a 9" x 6" x 1/8 inch aluminum cavity mold. The mold was flushed with nitrogen and heated to 60°C. The cocatalyst solution was then introduced. There was an immediate exotherm which peaked after 45 seconds at about 150°C. After cooling, the mold was opened to reveal a hard, completely solidified glass fiber reinforced plaque weighing 123.8 g, approximately 33% by weight glass fiber.

20

Example 3

25

Preparation of Coated Glass Fiber

30 Four milliliters of tetra-n-butylin was dissolved in 200 ml methylene chloride. A section of woven glass fiber roving was placed in an oven at 615°C and baked for 30 minutes after which it was cooled and weighed. The purpose of this baking procedure was to remove the sizing agents. The mat, weighing 58 g, was dipped into the above-described cocatalyst solution in air for approximately 30 seconds and allowed to air dry to a constant weight of 60.40 g indicating that the glass fiber mat had adsorbed 2.4 g of the tetrabutyltin cocatalyst.

35

Preparation of Catalyst Solution

36 To a 92.5/7.5 mixture of DCPD and ENB (160 g) under nitrogen was added 8 ml of silicon tetrachloride as a 0.25 molar solution in a DCPD/ENB mixture and tridodecylammonium molybdate ($[(\text{C}_{12}\text{H}_{25})_3\text{NH}]_2\text{Mo}_8\text{O}_{26}$) in amount of 4 ml of a 0.1 normal solution in 92.5/7.5 DCPD/ENB mixture.

40

Polymerization

45 The section of cocatalyst-coated glass fiber mat was placed into a 9" x 7 1/2" x 1/8 inch aluminum cavity mold. The mold was flushed with nitrogen and heated to 60°C. The catalyst solution was then introduced. There was an immediate exotherm which peaked after approximately 3 minutes at 172°C. After cooling, the mold was opened to reveal a hard, highly converted glass fiber reinforced plaque with no voids evident weighing 165.0 g, indicating a glass fiber loading of about 35%.

50

Example 4

55

Preparation of Coated Glass Fiber

Four milliliters of tetra-n-butylin and 2.0 g tridodecylammonium molybdate were dissolved in 200 ml

5 methylene chloride. A section of woven glass fiber roving was placed in an oven at 615°C and baked for 30 minutes after which it was cooled and weighed. The mat, weighing 55.5 g, was dipped into the above-described solution in air for approximately 45 seconds and allowed to air dry to a constant weight of 57.6 g indicating that 2.1 g of the catalyst and cocatalyst had been adsorbed onto the glass fiber.

5

Polymerization

10 Silicon tetrachloride in amount of 8 ml of a 0.25 molar solution in 92.5/7.5 DCPD/ENB mixture was added under nitrogen to 160 g of a DCPD/ENB 92.5/7.5 mixture. The above described coated glass fiber mat was placed into a 9" x 7 1/2" x 1/8" aluminum cavity mold. The mold was flushed with nitrogen and heated to 60°C at which time the monomer SiCl_4 solution was added. On opening the mold, it was observed that polymerization had occurred but that conversion was not complete in the center of the plaque indicating that the catalyst/cocatalyst was not homogeneously dispersed throughout the mat. This problem 15 can be overcome by using a longer dipping time or by using a more concentrated solution of the catalyst and cocatalyst.

15

Example 5

20

Catalyst Solution Preparation

25 A. 0.10 g WCl_6 was dissolved in 49 ml toluene under nitrogen.
 B. 0.04 g p-tert-butylphenol was dissolved in 10 ml toluene.
 C. Solutions or dispersions A and B were combined and purged with nitrogen for 2 hours to remove HCl liberated.
 D. 0.028 ml of benzonitrile was added to C to prepare the catalyst solution.

30

Preparation of Cocatalyst Solution

One and one-half milliliters di-butyl ether was added to 129 ml DCPD to which had already been added 10.8 ml of a 0.5 molar solution of DEAC in a 92.5/7.5 DCPD/ENB solution.

35

Glass Fiber

40 50 g of commercially available silane-sized, chopped strand fiberglass was introduced into a clean, dry sample bottle which was placed in an oven at 140°C for 12 hours and then allowed to cool under nitrogen.

Preparation of Coated Glass Fiber

45 One half of the catalyst solution (D) was added to the test bottle containing the chopped glass strands and toluene was removed by evaporation to afford the glass coated with the catalyst.
 Thirty two grams activator/monomer solution was injected under nitrogen into the test bottle containing glass strands coated with the catalyst. An immediate reaction followed as witnessed by a small exotherm. The bottle was placed in an oven at 105°C to drive the reaction to completion. After completion of the 50 polymerization, the color of the catalyst had changed from red to brown and the polymer took the form of a hard mass in which the chopped glass fiber strands were firmly embedded.

Example 6

55

The remaining half of catalyst solution D described in Example 5 was added to a second test bottle containing a further 50 g of chopped glass strands and toluene was removed by evaporation. The contents

of the bottle, which contained glass fiber strands coated with catalyst were then exposed to air and moisture by opening the bottle and exposing the contents to the atmosphere for a period of 72 hours at ambient conditions. After this period, the color of the coated glass had changed from red to brown. The bottle was then restoppered and 32 g of the activator/monomer solution was added at ambient temperature after which 5 the bottle was placed in an oven at 140 °C for a total of 120 minutes. The greatest portion of the mass had solidified to afford a blue-colored mass but there was a little unconverted yellow liquid which formed a separate upper layer indicating that this particular catalyst system, in contrast to the air-stable halogen-free metallate systems exemplified in examples 1 to 4, exhibits a certain degree of air-sensitivity even when adsorbed on to a glass-fiber support.

10

Example 7

15

Aqueous Dispersion of Molybdate Catalyst

Two grams of tristridecylammonium molybdate was dissolved in 5 grams of methyl isobutyl ketone. Deionized water in amount of 100 g was added to form a dispersion of catalyst.

20

Preparation of Coated Mat

A piece of Owens Corning 8608 glass fiber mat (about 13 μ fiber thickness) was dipped into the above 25 solution for about 15 seconds, removed, and then dried in an air oven at 150 °C for 30 minutes. The initial mat was white in color. The coated mat was uniformly light yellow in color, demonstrating that the mat was coated with catalyst.

30

Polymerization

Two layers of the above mat were cut to fit into a 6" x 9" x 1/8" aluminum cavity mold which was heated to about 60 °C. The mold was purged with nitrogen and then the cocatalyst activator solution of 35 Example 2 was introduced into the mold. The reaction was monitored by observing the temperature of the reaction mass. After the reaction mass had cooled in the mold, a completely solidified fiber reinforced plaque was removed from the mold.

Example 8

40

Preparation of Catalyst and Film Former Sizing Dispersion

45 One gram of tristridecylammonium tungstate was mixed with 5 g toluene, 15 g isopropanol, and 5 g Ricon 156 resin. Ricon 156 resin is a poly(styrene-butadiene) resin supplied by Colorado Chemicals. Also, 100 g of deionized water was added with vigorous mixing to create a dispersion.

50

Preparation of Treated Fibers

A 55 g portion of the sizing dispersion prepared above was mixed with 30 g of water-sized chopped fibers supplied by Owens Corning Fiberglas. The fibers were then dried for one hour in an air oven at 150 °C, and then over night at 50 °C.

55

Polymerization

About 15 grams of treated fibers were placed in a jar under nitrogen at room temperature. Sufficient cocatalyst solution was added to the fibers, as described in example 2. No reaction was observed at room temperature after several minutes. But when the jar was placed in an oil bath at 80°C, polymerization with an exotherm above 150°C occurred within four minutes. Conversion of monomer to polymer was judged to be high based on the hardness of the reaction mixture upon cooling.

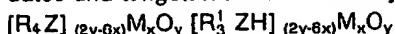
Claims

1. Substrate having on its surface a coating selected from the group consisting essentially of ring opening metathesis catalysts, ring opening metathesis cocatalysts, and mixtures thereof.
2. Substrate of claim 1 wherein said metathesis catalyst is selected from the group consisting essentially of halides, oxides, and oxyhalides of tungsten, molybdenum and tantalum; organoarsonium, organophosphonium, and organoammonium molybdates and tungstates, heteropolymolybdates, heteropolytungstates; and mixtures thereof.
3. Substrate of claim 2 wherein said metathesis cocatalyst is selected from the group consisting essentially of organoaluminums, organic tin compounds, organic lead compounds, and mixtures thereof.
4. Substrate of claim 2 wherein said organoammonium, organoarsonium, and organophosphonium molybdates and tungstates are defined by the following formula:
5. Reinforcing or filler material of claim 2 wherein said cocatalyst is air-insensitive and is selected from the group consisting essentially of organic tin compounds, organic lead compounds, and mixtures thereof.
6. Reinforcing or filler material of claim 5 wherein said cocatalyst is selected from the group consisting essentially of tetraalkyltins, trialkyltins hydrides, tetraalkylleads, and mixtures thereof.
7. Reinforcing or filler material of claim 6 wherein said cocatalyst is selected from the group consisting essentially of tetrabutyltin, tributyltin hydride, tetraethyllead; and mixtures thereof.
8. Substrate of claim 3 wherein said organoaluminums are defined by the following formulas:
$$(R_nMO)_a R_b^1 AlX_c \text{ and } (RO)_a R_b^1 AlX_c$$

where M is selected from silicon, tin, germanium, lead, and aluminum, R and R¹ are individually selected from lower alkyl groups and phenyl groups, X is a halide selected from chloride and iodide, the sum of a, b and c is 3.0 with each parameter denoting the equivalents of the moieties in the cocatalyst.

9. Substrate of claim 4 wherein said substrate is selected from the group consisting essentially of glass fibers, aramid fibers, graphite fibers, and mixtures thereof.
10. Substrate of claim 1 wherein said catalyst is selected from tungsten hexachloride, tungsten oxytetrachloride, tungsten oxide, tridodecylammonium tungstate, methyltricaprylammonium tungstate, tri(tridecyl)ammonium tungstate, trioctylammonium tungstate, molybdenum pentachloride, molybdenum oxytrichloride, tridodecylammonium molybdate, methyltricaprylammonium molybdate, tri(tridecyl)ammonium molybdate, trioctylammonium molybdate, and tantalum pentachloride; wherein said cocatalyst is selected from diethylaluminum halides, propoxyethylaluminum halides, tetrabutyl tin hydride, triphenyltin hydride, diethylaluminum hydride, triethyltin hydride, tripropyltin hydride, tetraethyltin, tetrabutyltin, and mixtures thereof; and wherein said substrate is selected from glass fibers, aramid fibers, graphite fibers, and mixtures thereof.
11. Substrate of claim 2 wherein said cocatalyst is selected from diethylaluminum chloride, diethylaluminum iodide, and mixtures thereof; said cocatalyst is used with a reaction rate moderator selected from ethers, esters, ketones, alcohols, and mixtures thereof, wherein molar ratio of said moderator to said cocatalyst is 1:1.5 to 1:5.
12. Method of preparing a substrate with a coating thereon selected from ring-opening metathesis catalysts, ring-opening metathesis cocatalysts, and mixtures thereof, comprising applying said coating onto said substrate, and drying said substrate.
13. Method of claim 12 wherein said metathesis catalyst is selected from the group consisting essentially of halides, oxyhalides and oxides of tungsten, molybdenum and tantalum; organoarsonium, organophosphonium, and organoammonium molybdates and tungstates; heteropolymolybdates, heteropolytungstates; and mixtures thereof; and wherein said metathesis cocatalyst is selected from the group consisting essentially of organoaluminums, organic tin compounds, organic lead compounds, and mixtures thereof.

14. Method of claim 12 wherein said organoammonium, organoarsonium and organophosphonium molybdates and tungstates are defined by the following formula:



where Z is nitrogen, arsenic or phosphorus, M is molybdenum or tungsten, O is oxygen, x and Y represent the number of M and O atoms in the molecule based on the valence of +6 for molybdenum, +6 for tungsten and -2 for oxygen, and R and R¹ are individually selected from hydrogen, alkyl and alkylene groups of 1 to 20 carbon atoms, and cycloaliphatic groups each of 5 to 16 carbon atoms.

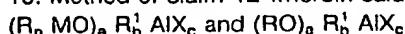
15. Method of claim 13 comprising applying said coating from an aqueous sizing composition which comprises an organosilane, lubricant, antistatic agent, film forming resin, said coating, and water.

16. Method of claim 12 wherein said coating is dissolved in at least one norbornene-type monomer, and said norbornene-type monomer is selected from the group consisting essentially of norbornene, methylnorbornene, vinyl norbornene, ethyldienenorbornene, tetracyclododecene, methyltetraacyclododecene, dicyclopentadiene, trimers of cyclopentadienes, tetramers of cyclopentadienes, and mixtures thereof.

17. Method of claim 12 wherein amount of said metathesis catalyst and/or cocatalyst is 0.1 to 0.7 weight part per 100 weight parts of said at least one norbornene-type monomer.

18. Method of claim 16 wherein said substrate is a glass fiber mat and said coating is applied to said mat by dipping said mat in an aqueous medium containing said coating.

19. Method of claim 12 wherein said organoaluminums are defined by the following formulas:



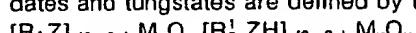
20. Method of claim 12 wherein M is selected from silicon, tin, germanium, lead, and aluminum, R and R¹ are individually selected from lower alkyl groups and phenyl groups, X is a halide selected from chloride and iodide, the sum of a, b and c is 3.0 with each parameter denoting the equivalents of the moieties in the cocatalyst; wherein said catalyst is selected from tungsten hexachloride, tungsten oxytetrachloride, tungsten oxide, tridodecylammonium tungstate, methyltricaprylammonium tungstate, tri(tridecyl)ammonium tungstate, trioctylammonium tungstate, molybdenum pentachloride, molybdenum oxytrichloride, tridodecylammonium molybdate, methyltricaprylammonium molybdate, tri(tridecyl)ammonium molybdate, trioctylammonium molybdate, and tantalum pentachloride; and wherein said substrate is selected from glass fibers, aramid fibers, graphite fibers, and mixtures thereof.

21. Method of claim 11 wherein said cocatalyst is selected from diethylaluminum halides, propoxyethylaluminum halides, tetrabutyl tin hydride, triphenyltin hydride, trimethyltin hydride, triethyltin hydride, tripropyltin hydride, tetraethyltin, tetrabutyltin, and mixtures thereof.

22. Process of preparing a reinforced molded article comprising placing into a mold a substrate having thereon a component of a ring-opening metathesis catalyst system selected from the group consisting essentially of catalyst and cocatalyst, introducing into the mold at least one norbornene-type monomer, allowing ring opening polymerization reaction by ring opening of said at least one norbornene-type monomer to proceed in the mold, and extracting from the mold said molded article.

23. Process of claim 21 wherein said catalyst is selected from halides, oxyhalides and oxides of tungsten, molybdenum and tantalum; organoarsonium, organophosphonium and organoammonium molybdates and tungstates; heteropolymolybdates; heteropolytungstates; and mixtures thereof; and wherein said cocatalyst is selected from organoaluminums, organotin compounds, organolead compounds, and mixtures thereof.

24. Process of claim 21 wherein said organoaluminums are defined by the following formulas:



25. Method of claim 24 wherein M is selected from tin, lead, and aluminum, R and R¹ are individually selected from lower alkyl groups and phenyl groups, X is a halide selected from chloride and iodide, and the sum of a, b and c is 3.0 with each parameter denoting the equivalents of the moieties in the cocatalyst; wherein said organotin compounds are selected from air-insensitive tetralkyltins and air-insensitive trialkyltin hydrides; and said organic lead compounds are selected from the group consisting essentially of air-insensitive tetraalkyllead compounds.

26. Process of claim 24 wherein said substrate is selected from the group consisting essentially of glass fibers, aramid fibers, graphite fibers, and mixtures thereof; said process also including the step of introducing with said cocatalyst a halogen source selected from chlorosilanes.

26. Process of claim 24 wherein amount of catalyst is 0.05 to 1 weight part per 100 weight parts of said at least one norbornene-type monomer; wherein molar ratio of said cocatalyst to said catalyst is 0.1 to 200; and wherein said amount of said halogen source is 0.1 to 2 millimoles per mole of said monomer(s).

27. Process of claim 25 wherein said norbornene-type monomer is selected from substituted and unsubstituted 2-norbornenes, dicyclopentadienes, dihydrodicyclopentadienes, trimers of cyclopentadienes, tetramers of cyclopentadienes, tetracyclododecenes, and mixtures thereof.

5 28. Process of claim 25 wherein said norbornene-type monomer is selected from norbornene, methylnorbornene, vinyl norbornene, ethylidenenorbornene, tetracyclododecene, methyltetracyclododecene, dicyclopentadiene, trimer of cyclopentadiene, tetramer of cyclopentadiene, and mixtures thereof; and

10 10 wherein said cocatalyst is selected from diethylaluminum halides, propoxyethylaluminum halides, tetrabutyltin hydride, triphenyltin hydride, trimethyltin hydride, triethyltin hydride, tripropyltin hydride, tetraethyltin, tetrabutyltin, and mixtures thereof.

15 29. Process of claim 27 wherein said halogen source is tetrachlorosilane; wherein said catalyst is selected from the group consisting essentially of tungsten hexachloride, tungsten oxytetrachloride, tungsten oxide, tridodecylammonium tungstate, methyltricaprylammonium tungstate, tri(tridecyl)ammonium tungstate, trioctylammonium tungstate, molybdenum pentachloride, molybdenum oxytrichloride, tridodecylammonium molybdate, methyltricaprylammonium molybdate, tri(tridecyl)ammonium molybdate, trioctylammonium molybdate, and tantalum pentachloride; and wherein said substrate is selected from the group consisting essentially of glass fibers, aramid fibers, graphite fibers, and mixtures thereof.

20

25

30

35

40

45

50

55



(19) Eur pâisches Pat ntamt
European Patent Office
Office uropéen des br vets



(11) Publication number:

0 424 833 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90120173.1

(51) Int. Cl. 6: C08J 5/04, C08G 61/08

(22) Date of filing: 20.10.90

(30) Priority: 24.10.89 US 426390

(71) Applicant: THE B.F. GOODRICH COMPANY
3925 Embassy Parkway
Akron Ohio 44313-1799(US)

(43) Date of publication of application:
02.05.91 Bulletin 91/18

(72) Inventor: Goodall, Brian L.
3959 Clover Hill Road
Akron, Ohio 44313(US)
Inventor: Standish, John V.
4615 Broadale Road
Cleveland, Ohio 44109(US)

(36) Designated Contracting States:
BE DE DK FR GB IT NL SE

(45) Date of deferred publication of the search report:
08.01.92 Bulletin 92/02

(74) Representative: von Kreisler, Alek,
Dipl.-Chem. et al
Patentanwälte Von Kreisler-Setting-Werner,
Delchmannhaus am Hauptbahnhof
W-5000 Köln 1(DE)

(57) Coated reinforcing material.

(57) This invention pertains to a substrate having thereon a coating of a metathesis catalyst and/or cocatalyst, to a method for applying such a coating to the substrate, and to a process for producing a molded product by placing into a mold a substrate having thereon a coating of the metathesis catalyst and/or cocatalyst, introducing into the mold at least one norbornene-type monomer, polymerizing the monomer in presence of the metathesis catalyst system, and extracting the molded article from the mold wherein the monomer(s) is polymerized to a thermoset or crosslinked polymer.



European
Patent Office

EUROPEAN SEARCH
REPORT

Application Number

EP 90 12 0173

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 226 957 (THE B.F. GOODRICH CO.) * Claims 1-20 - - -	1-29	C 08 J 5/04 C 08 G 61/08
A	EP-A-0 107 079 (THE B.F. GOODRICH CO.) * Claims 1-11 - - -	1-29	
A	US-A-4 380 617 (MINCHAK et al.) * Claims 1-10 - - -	1-29	
A	EP-A-0 311 809 (NIPPON ZEON K.K.) * Claims 1-4 - - - -	1-29	
TECHNICAL FIELDS SEARCHED (Int. Cl.8)			
C 08 G C 08 J			

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	11 October 91	GLANDDIER A.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
non-written disclosure
intermediate document
theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date

D: document cited in the application

L: document cited for other reasons

&: member of the same patent family, corresponding document